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Simple Topological Estimation of the First Electronic Hyperpolarizability of Polymethine Compounds

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Topological characteristics of end groups of polymethine compounds have been revealed which govern the value of the first electronic hyperpolarizability and are easily obtainable in the long polymethine chain approximation. For a variety of π-conjugated organics, they are represented in a table permitting prediction of compounds with pronounced nonlinear optical properties. The theoretical estimates of β are shown to correlate well with experimentally observed values.

The past two decades have witnessed a vigorous development of nonlinear optical materials and increasing theoretical efforts directed to the rationalization of observed molecular hyperpolarizabilities.[1,2] At the same time, progressively intensive computational strategies, up to *ab initio* level, are involved in the prediction of nonlinear optical responses for a variety of molecular structures. However, from the extensive literature on the subject (see references cited in refs 1 and 2) it is seen that even the most potent quantum chemical techniques often approximate hyperpolarizabilities within half an order of magnitude. This sends theorists in search of the simple methods which would enable estimation of optical nonlinearities and reveal fundamental characteristics governing trends in their values. Such qualitative models show considerable promise for an understanding of intimate regularities of relationships between chemical constitution and nonlinear optical properties. The earliest analysis of this kind dates back to the concept of the equivalent internal field,[3] intended for treatment of the first hyperpolarizability, β, of substituted benzenes; subsequently it was generalized by Marder and collaborators.[4,5]

The present paper puts forward another approach to modeling the second-order nonlinearity for polymethine compounds. On the topological basis, using the Hückel Hamiltonian, it involves modern Green's function formalism and, following Lifshits' theory,[6] provides an analytical description for the shifts of individual energy levels of a quasicontinuous spectrum of a large system perturbed by locally attached fragments.[7] A related method called the long polymethine chain approximation was developed to treat quasilinear π-conjugated systems.[8,9] On the whole, this line of study of polymethine compounds yielded an adequate understanding of their chemical and optical behavior.[10] A notable simplification resulting from ignoring interelectron repulsion enabled keeping the analytical character for the treatment of polymethine compounds with arbitrary end groups. This comprises a principal distinction of the model in question from most of accepted quantum chemical methods (as for instance used in ref 11) providing higher accuracy but at a sacrifice in generality.

Recently it was invoked to account for a nonmonotonic dependence of the first hyperpolarizability of polymethines on the donor−acceptor strength of their end groups.[12] Here it is our intention to reveal certain end-group topological parameters which appear to be crucial in determining β-values.

As a fundamental characteristic of an end group, we use its inverse topological matrix also referred to as Green's function matrix. Notably, the consideration can be restricted to the matrix element which corresponds to the end-group atom bound to the polymethine chain:

$$g_j(z) = \langle b_j|(z\cdot 1 - \mathbf{H}_j)^{-1}|b_j\rangle \qquad (1)$$

(z is a dimensionless energy variable; $j = 1, 2$ labels two end groups attached to the chain through their b_jth atoms, $\mathbf{H}_j$ is an end-group Hamiltonian). In refs 7−10, it was demonstrated that the frontier level positions for a polymethine compound were unambiguously determined by two specific functions, $F(z)$ and $L(z)$, defined in terms of the function $g_j(z)$ as follows:[10]

$$F(z) = \sum_{j=1}^{2} F_j(z) \qquad F_j(z) = \frac{1}{\pi}\,\mathrm{arcctg}\,\frac{1 + g_j(z)\cos\theta}{g_j(z)\sin\theta} \qquad (2)$$

$$L(z) = -2\pi\sin\theta\cdot F'(z) \qquad \theta = \arccos(-z/2)$$

(Hereafter, we shall use primed letters to designate derivatives of the corresponding quantities with respect to the energy variable z). The values $F(0)$ and $L(0)$ (further denoted as F and L) account for end-group effects respectively on the position of the molecular energy gap relative to the Fermi level ($z = 0$) and its magnitude; they are regarded as end-group contributions to the electron-donor ability and effective length of a polymethine molecule. Redox properties of a molecule constituted by N-methine chain ($N = k + 2n$; $k = 0$ or 1, and n is an integer) and two end groups, M_1 and M_2, are governed by the total quantity $F_{tot} = \{F_1 + F_2 + (k - 1)/2\}$ ($\{...\}$ designates taking fractional part of a number). The closer to 0.5 is F_{tot}, the more stable is the corresponding molecule with respect to reducers and oxidizers, whereas it tends to accept electrons at $0 < F_{tot} < {}^1/_2$ and to donate them at ${}^1/_2 < F_{tot} < 1$. The wavelength of the first electronic transition of the polymethine molecule is proportional to the value $N + 1 + L$. Thus L characterizes an effective lengthening of a polymethine chain caused by end groups.

As shown previously,[12] the topological parameters mentioned and their derivatives taken at $z = 0$ are related to the key parameters specifying the β value in the context of a simple

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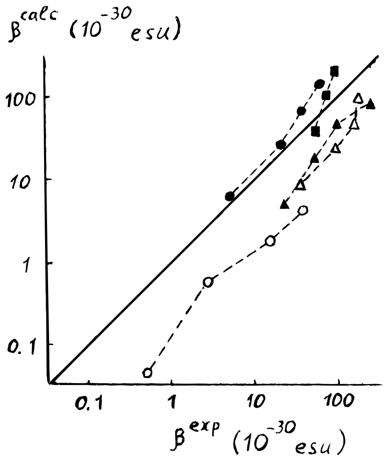


Figure 1. Correlation between calculated, β^{calc}, and experimental,[18,19] β^{exp}, static first hyperpolarizabilities for vinylogous series ($n = 0, 1$, etc., from left to right) of polymethine compounds M_1-C_{k+2n}-M_2 where M_1 and M_2 are end-group numbers in Table 1: (○) 1-C_{1+2n}-2, (●) 5-C_{1+2n}-2, (△) 5-C_{2+2n}-3, (▲) 5-C_{1+2n}-4, (■) 5-C_{2+2n}-7.

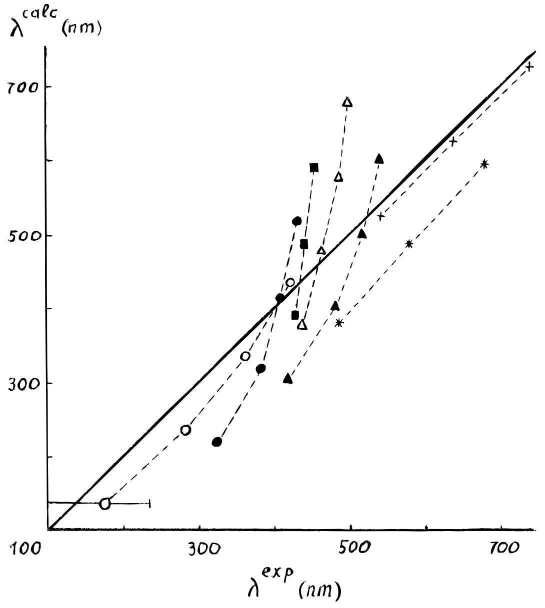


Figure 2. Correlation between calculated, λ^{calc}, and experimental,[18−21] λ^{exp}, wavelengths of the first electronic transition for compounds treated in Figure 1 as well as for symmetrical polymethines: (+) 9-C_{3+2n}-9, (*) 10-C_{3+2n}-10.

two-state model,[13,14] which is best applicable to dipolar quasi-linear molecules (contributions to β other than the dipolar one were discussed in detail in ref 15):

$$\beta = 3\Delta\mu\cdot\mu_{ge}^{2}/E_{ge}^{2} \qquad \Delta\mu = \mu_{ee} - \mu_{gg} \tag{3}$$

$$E_{ge} = 2\pi|\beta_{cc}|(N + 1 + L)^{-1}$$

$$\mu_{ge} = -(2/\pi^2)er_{cc}(N + 1 + L)$$

$$\Delta\mu = \pi e r_{cc}(N + 1)(N + 1 + L)^{-2}(L_2' - L_1') \tag{4}$$

Here $\Delta\mu$ is the difference in dipole moments between the ground (g) and the first excited (e) states which is proportional to the difference of the effective length derivatives for two end groups, $L_2' - L_1'$; E_{ge} and μ_{ge} are, respectively, the energy and the dipole moment matrix element for a g → e transition; $\beta_{cc} \simeq -4$ eV is the resonance integral for a C−C bond within the N-methine chain; e is the electronic charge, $r_{cc} \simeq 1.247$ Å is the projection of a chain C−C bond onto the long molecular axis. On substituting eqs 4 into formula 3, we arrive at the following relation for β:

$$\beta = \frac{3}{\pi^5}\frac{e^3 r_{cc}^{\ 3}}{\beta_{cc}^{\ 2}}(N + 1)(N + 1 + \mathrm{L})^2(L_2' - L_1') \tag{5}$$

Interestingly, the same expression is derivable from the corresponding L dependence of the linear polarizability:

$$\alpha = 2\frac{\mu_{ge}^{\ 2}}{E_{ge}} = \frac{4}{\pi^5}\frac{e^2 r_{cc}^{\ 2}}{|\beta_{cc}|}(N + 1 + L)^3 \tag{6}$$

if we assume the existence of the effective internal field, E_{eff}, induced by the donor and acceptor end groups.[5] In fact, if the total dipole moment of a molecule placed in an external electric field, E, is defined as $\mu(E_{eff},E) = \mu_0(E_{eff}) + \alpha(E_{eff})E + \beta(E_{eff})E^2 + ...$, then $\beta(E_{eff}) = {}^1/_2\ \partial\alpha(E_{eff})/\partial E_{eff}$. The effective internal field arises from the difference in potentials between two end groups, $\Delta\varphi = (N + 1)r_{cc}E_{eff}$. This can be simulated by oppositely varying the energy parameter z at the end groups. With $\Delta z = e\Delta\varphi/(2|\beta_{cc}|)$ added to and subtracted from $z = 0$ for the two end groups, the total effective length, L, which enters into eq 6 can be represented as $L_1(-\Delta z) + L_2(\Delta z)$, and differentiating eq 6 with respect to E_{eff} leads to

$$\beta = \frac{6}{\pi^5}\frac{e^2 r_{cc}^{\ 2}}{|\beta_{cc}|}(N + 1 + L)^2\frac{dL}{dE_{eff}} \tag{7}$$

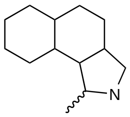
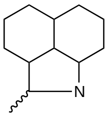
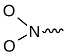
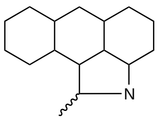
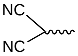
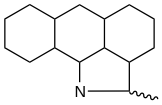
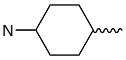
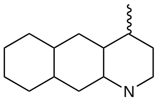
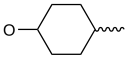
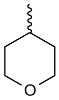
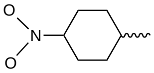
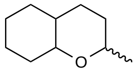
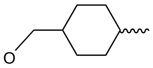
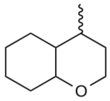
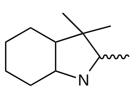
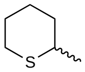
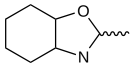
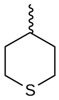
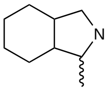
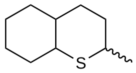
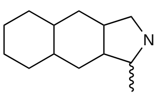
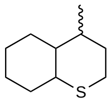
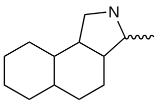
where

$$\frac{dL}{dE_{eff}} = (L_2' - L_1')\frac{d(\Delta z)}{dE} = \frac{e r_{cc}(N+1)}{2|\beta_{cc}|}(L_2' - L_1') \tag{8}$$

Substituting eq 8 into eq 7 immediately yields formula 5. Notably, in the treatment of the first hyperpolarizability for a polymethine compound, we focus on the end groups and not on the polymethine chain itself as the latter provides no contribution to this nonlinear optical parameter due to symmetry factors (see, e.g. ref 16).

The consistency of two approaches, the long polymethine chain approximation (see eqs 5 and 6) and effective-field model, provides support for the view that the end-group topological parameters L and L' are the sought-for factors determining trends in the first hyperpolarizability. For symmetric compounds, the β value vanishes in terms of the model used, since $L_2' = L_1'$ in eq 5; this is in complete agreement with the results reported by Marder et al. based on the treatment of bond-order alternation which reduces to zero in this case.[5] For unsymmetric polymethine molecules, a nonzero bond-order alternation (giving rise to a nonzero β, according to ref 5) results within the framework of the long-chain approximation despite the assumption of equal resonance integrals for chain C−C bonds.[17] At the same time, focusing on the topological parameters involved in eq 5 one can infer that high β values should be anticipated for the polymethine compounds whose end groups are characterized by the sufficiently great quantities $L_1 + L_2$ and $|L_2' - L_1'|$. In Table 1, the parameters F, L, and L' are presented for a number of end groups of polymethine compounds studied spectroscopically.[18−21] The table also includes 16 end groups having $L > 3$ and $|L'| > 4$ and thus showing promise as to their nonlinear optical response which have been selected out of 50 residues usually involved in polymethine chemistry. In the calculation of the topological characteristics of interest, we used parametrization as indicated in the note to Table 1. It should

TABLE 1: Topological Parameters of End Groups Common in Polymethine Chemistry

no.	M_j	F	L	L'	no.	M_j	F	L	L'
1		0.250	0.500	0	14		0.163	3.564	−5.359
2		0.148	0.200	0.120	15		0.750	5.500	12.000
3		0.747	2.451	−3.818	16		0.750	8.625	40.109
4		0.199	1.948	−1.486	17		0.750	8.625	24.141
5		0.078	2.176	−2.830	18		0.837	3.617	6.694
6		0.040	1.677	−0.773	19		0.789	3.001	4.884
7		0.077	2.596	−6.772	20		0.699	3.741	5.404
8		0.852	4.200	15.880	21		0.699	3.969	5.496
9		0.250	3.250	−1.313	22		0.736	4.602	6.051
10		0.837	1.873	−0.873	23		0.736	4.602	8.043
11		0.215	4.244	−5.660	24		0.651	4.907	5.000
12		0.290	6.054	−9.500	25		0.651	5.046	4.470
13		0.163	3.849	−4.741					

Note: Only σ-bonds are indicated in end-group structural formulae. The Coulomb, α_X, and the resonance, $\beta_{XX'}$, integrals for atoms and bonds are defined respectively as $\alpha_C + h_X\beta_{CC}$ and $\eta_{XX'}\beta_{CC}$ with commonly used h_X and $\eta_{XX'}$ values: $h_C = 0$, $h_N = 1$, $h_O = 2$, $h_S = 0.7$; $\eta_{CC} = \eta_{CN} = 1$, $\eta_{CO} = 0.8$, $\eta_{CS} = 0.4$; for nitro groups in structures 3 and 7, $h_N = 2$, $h_O = 1$, $\eta_{NO} = 0.7$; for cyano groups in 4, $\eta_{CN} = 1.2$, for exocyclic oxygen atoms in 2, 6, and 8, $\eta_{CO} = 1$.

be pointed out that the choice of parameters causes the strongest effect on high-order derivatives of $F(z)$ such as $L'(z)$. The factor L' determining β values accounts for dramatic discrepancies between experimentally measured hyperpolarizabilities and their estimates yielded by semiempirical methods.

The calculated by eq 5 versus observed[18,19] β values are presented in Figure 1 which shows a reasonable accordance between them: Points are clustered along the bisector of the first coordinate angle thus suggesting that theoretical expectations of high β values are corroborated experimentally and Table 1 can be helpful in the molecular design of polymethine compounds with a pronounced optical nonlinearity. Their redox properties are also controllable by the selection of end groups with the appropriate values of topological electron-donor ability. To exemplify, for real polymethine compounds shown in Figure 1, F_{tot} varies in the range from 0.23 to 0.66 thus not deviating widely from the optimum value, 0.5. A surprising adequacy of the calculated β values appears to result from the primary part of molecular topology in the origin of optical nonlinearity for the compounds under study. That is why a model neglecting both the electron−electron repulsion and bond resonance integral alternation in the polymethine chain does account for certain substantial features of molecular spectral behavior.

It can be noticed in Figure 1 that within certain vinylogous series of polymethine compounds, theoretical estimates of β increase with N faster than the corresponding experimental values. This is evidently due to the emergence of a finite gap at $N \rightarrow \infty$ in the energy spectrum of polymethines, which fact is ignored in the long-chain approximation. The gap magnitude is governed by the quantity $\Delta F = \{F_1 - F_2 + (k-1)/2\}$, and the effect reaches its maximum at $\Delta F = 0.5$. Indeed, as seen from Figure 2, the derivative $d\lambda^{\text{theor}}/d\lambda^{\text{exp}}$ increases in the following series of molecules: 9-C_{3+2n}-9, 10-C_{3+2n}-10, 1-C_{1+2n}-2, 5-C_{1+2n}-4, 5-C_{1+2n}-2, 5-C_{2+2n}-3, and 5-C_{2+2n}-7, whose ΔF values amount respectively to: 0, 0, 0.10, 0.12, 0.07, 0.17, and 0.50. Accordingly, for unsubstituted chains containing an even number of carbon atoms and characterized by $\Delta F = 0.5$ (i.e. for so-called ideal polyenes), the results of minimizing the ground-state energy suggested that an antiferromagnetic state with a gap became preferable to the gapless one at $N \geq 10$.[22] Also, the value ΔF serves as a quantitative measure of polymethinic or polyenic molecular nature treated by Dähne.[23] It becomes therefore apparent that the mentioned trend in β values within vinylogous series will be marked the more, the closer are the compounds to ideal polyenes.

To sum up, a simple model for estimating the first hyperpolarizability of polymethine compounds is developed which analytically treats the factors determining β values. These easily calculable topological characteristics enable tendencies in β behavior to be revealed and thus facilitate a large-scale search and molecular design of conjugated compounds with a pronounced second-order optical nonlinearity.

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